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Integrated Approach to Acid Rainfall Assessments

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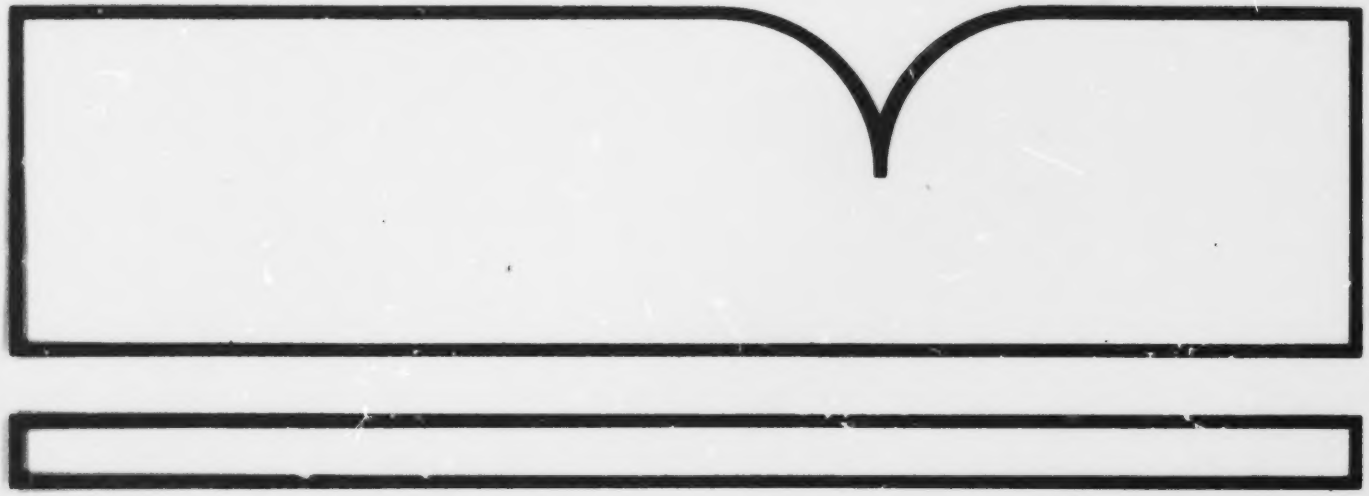

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16. ABSTRACT

A tiered approach to the mathematical modeling of acid precipitation, its fate and effects, might include: (1) a steady-state susceptibility model to assess long-term effects from average annual atmospheric loadings on surface and groundwaters; (2) a dynamic, regional model to assess the role of long-range versus point-source pollutant loadings for regulatory purposes and (3) a three-dimensional dynamic event model to assess the maximum environmental insult to a specific ecosystem during critical conditions such as a snow-melt event. An integrated approach is needed which considers the fate of pollutants from their origin through terrestrial and aquatic ecosystems to the ultimate water resource, groundwater. In this chapter, the first step, the steady-state model is developed and applied to northern Wisconsin, the Upper Wisconsin River Basin. An example of the dynamic problem including CO_2 gas exchange and equilibrium pH is also discussed.

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CHAPTER 13

AN INTEGRATED APPROACH TO ACID RAINFALL ASSESSMENTS

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INTRODUCTION

A tiered approach to the mathematical modeling of acid precipitation, its fate and effects, might include: (1) a steady-state susceptibility model to assess long-term effects from average annual atmospheric loadings on surface and groundwaters; (2) a dynamic, regional model to assess the role of long-range versus point-source pollutant loadings for regulatory purposes and (3) a three-dimensional dynamic event model to assess the maximum environmental insult to a specific ecosystem during critical conditions such as a snow-melt event. An integrated approach is needed which considers the fate of pollutants from their origin through terrestrial and aquatic ecosystems to the ultimate water resource, groundwater. In this chapter, the first step, the steady-state model is developed and applied to northern Wisconsin, the Upper Wisconsin River Basin. An example of the dynamic problem including CO_2 gas exchange and equilibrium pH is also discussed.

TRICKLE-DOWN MODEL

Conceptual Development

Figure 1 is a schematic of a compartmentalized fate and transport model for acid precipitation assessments. The driving force for the system is the natural and anthropogenic emissions of SO_x and NO_x. Other chemical emissions such as H_2S and N_2O may be oxidized relatively rapidly in the atmosphere. The model is a "trickle-down" system in which pollutants descend from the atmosphere to the terrestrial canopy where sorption and biotransformations occur. The terrestrial compartment includes the snow-pack (and its attendant deposition) as well as marshes and overland runoff water. Rivers and lakes are classified as surface waters. Terrestrial runoff water becomes tributary to lakes, and percolation results in surficial or water table aquifers. There may exist interflow between the surface water and surficial aquifers, or alternatively groundwater recharge of bedrock aquifers. Acid is neutralized by dissolution of calcerous overburden and other minerals, and leaching of nutrients or heavy metals is possible along the way.

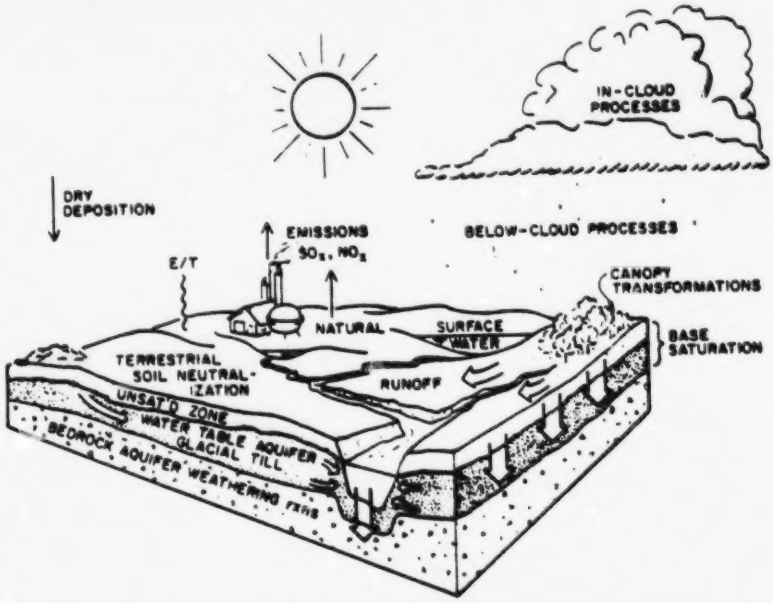
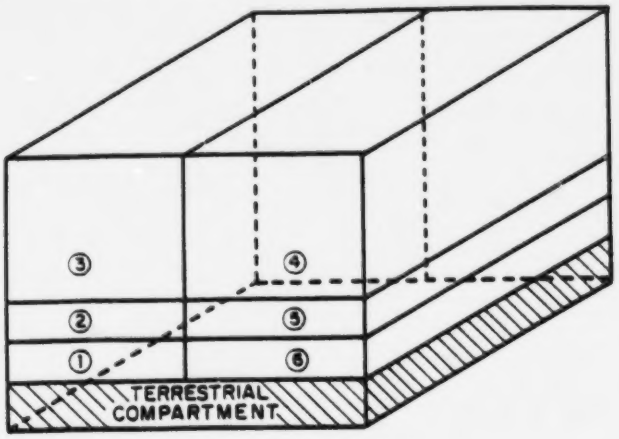


Figure 1. Schematic of compartmentalized fate and transport model for acid precipitation assessments. Compartments include clouds, below-clouds, canopy, soil layer, unsaturated zone, water table aquifer, surface lakes and streams, and bedrock aquifers.

Figure 2 depicts the transport of atmospheric pollutants through a number of interconnected compartments in the grid. Convection and dispersion connects the well-mixed boxes of volume, $V = \partial x \cdot \partial y \cdot H$, where ∂x and ∂y are the length and width of the cell, respectively, and H is the average mixing-layer height. Initially, the surface flux calculations are based on cell con-



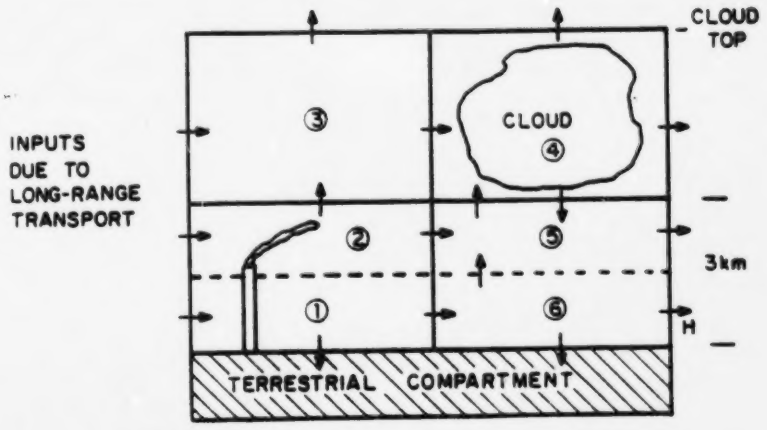


Figure 2. Interrelationship of atmospheric transport model and terrestrial compartment.

centrations determined from actual field data. Twenty-four-hour averaged SO_2, SO_4^{2-}, NO_3^- and TSP concentrations measured at monitoring stations in the vicinity of the study region have been compiled from existing data bases (e.g., EPRI/SURE, MAP3S, etc.) and are used to estimate 24-hr averaged concentrations within each cell. These concentrations are then used to calculate the amounts of SO_2, SO_4^{2-} and NO_3^- deposited to the surface in that 24-hr period. The dry deposition velocities of each cell are determined based on surface type and season, and the wet depositon rate within each cell varies with precipitation amount and duration. Seasonal and yearly loadings are then estimated as steady-state approximations. This analysis can be extended to other trace gases (e.g., NH_3).

To develop an accurate mass balance model for acidity transfers between the five compartments in the trickle-down model requires a good understanding of the geohydrology within each cell. Figure 3 presents a hypothetical hydrologic balance for the Rhinelander cell of a northern Wisconsin acid rainfall assessment. Assuming steady state, the sum of the inflows to each compartment must equal the sum of the outflows plus evapotranspiration. Annual rainfall and evaporation estimates can be obtained from raingauge and pan information: terrestrial runoff and percolation are derived from the rational formula: runoff = rainfall intensity x area x fraction percolated. Aquifer recharge and export (out of the cell) can be calculated from knowledge of the soils, confining layers and bedrock geology via the 2-D Darcy equation. Permeability constants, porosities, piezometric head and

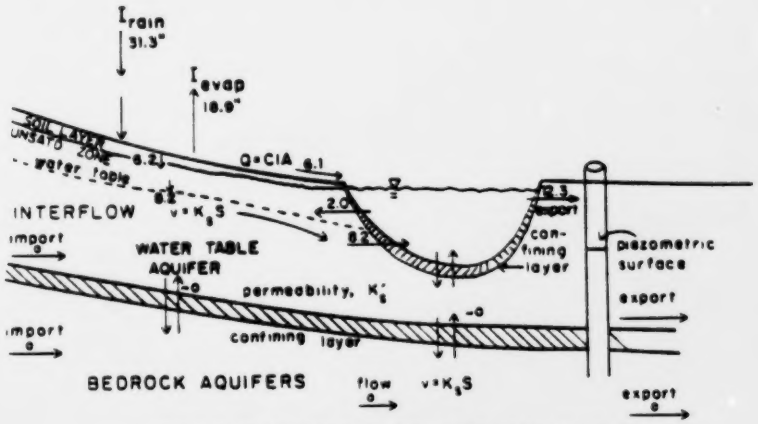


Figure 3. Hydrologic balance (in./yr) in trickle-down model.

aquifer dimensions are required for analysis. The hydrology of the system is critical to understanding both the steady state and the time response of the system.

Mass Balance Equations

The trickle-down model is based on the principle of mass continuity for alkalinity. Alkalinity is a conservative state variable which is not influenced by the exchange of CO_2 with the atmosphere. Negative alkalinity is free mineral acidity.

For each of the five compartments in the trickle-down model, an alkalinity mass balance equation is constructed according to Equation 1:

$$V_i \frac{dA_i}{dt} = \sum_{j=1}^{5} (Q_{i,j} A_j) - \sum_{j=1}^{5} (Q_{j,i} A_i) \pm \text{terms} \qquad (1)$$

Mass Accumulation	=	Sum of the Inputs	−	Sum of the Outflows	±	Sources or Sinks

where

V_i = volume of the i^{th} compartment (m^3)
$Q_{i,j}$ = flow from the j^{th} compartment into the i^{th} compartment (m^3/yr)
A_i = alkalinity of the i^{th} compartment (eq/m^3)
t = time (yr)

As a first approximation for northern Wisconsin, the pH and pCO_2 of the rainfall were known, which specifies the alkalinity and equilibrium chemistry for the system (CO_2, $CaCO_3$, and H_2O) according to Equation 2:

$$A = K_H (\alpha_1 + 2\alpha_2) (pCO_2/\alpha_0) + OH^- - H^+ \qquad (2)$$

where

A = alkalinity (eq/m^3)
K_H = Henry's law constant for CO_2
α_0 = $[H_2CO_3]/C_T$ = distribution coefficient
α_1 = $[HCO_3^-]/C_T$ = distribution coefficient
α_2 = $[CO_3^{-2}]/C_T$ = distribution coefficient
pCO_2 = partial pressure of CO_2 at 1 atmosphere = $10^{-3.5}$

Therefore, the system of five equations representing five compartments can be reduced to a system of four equations for four compartments and a specified wetfall and dryfall input. The average total sulfate load in the

Boundary Waters Canoe Area of Northern Minnesota has been reported as 11 kg/ha-yr by Glass and Loucks [1], and this figure has been used as an initial estimate of the total acid deposition. Best results were obtained with a sulfate loading of 24 kg/ha-yr, typical of northern Wisconsin.

The final system of mass balances for each compartment is presented in Equations 3-6.

Soil Compartment 2

$$V_2 \frac{dA_2}{dt} = Q_{2,1}A_1 + LA_{dry}\,(\%\ \text{terrestrial}) - Q_{4,2}A_2 - Q_{3,2}A_2 + k_2 M_2 V_2 (r_{eq_2} - r_2) - Q_{1,2}A_2 \quad (3)$$

Unsaturated Compartment 3

$$V_3 \frac{dA_3}{dt} = Q_{3,2}A_2 - Q_{5,3}A_3 + Q_{3,4}A_4 + k_3 M_3 V_3 (r_{eq_3} - r_3) \quad (4)$$

Surface Lakes Compartment 4

$$V_4 \frac{dA_4}{dt} = Q_{4,2}A_2 + Q_{4,5}A_5 - Q_{6,4}A_4 - Q_{3,4}A_4 + Q_{4,1}A_1 + LA_{dry}\,(\%\ \text{lakes}) \quad (5)$$

Water Table Aquifer Compartment 5

$$V_5 \frac{dA_5}{dt} = Q_{5,3}A_3 - Q_{4,5}A_5 + k_5 M_5 V_5 (r_{eq_5} - r_5) \quad (6)$$

Bedrock Aquifer Compartment 6

$$V_6 \frac{dA_6}{dt} = Q_{6,5}A_5 - Q_{5,6}A_6 - Q_{7,6}A_6$$

where

- L = dryfall acid loading (kg/yr as H^+)
- A_{dry} = dry deposition (eq/kg as H^+)
- k = rate constant for acid neutralization by soil (per year)
- M = specific density of soil in the overburden (kg/m^3)
- V = volume of the interflow compartment (m^3)
- r_{eq} = initial sum of the bases on the soil (eq/100 kg)
- r = cumulative base cation export or equivalents of acid neutralized by soil (eq/100 kg).

Compartment 1 is the atmosphere and compartment 7 refers to export out of the grid cell. In this preliminary analysis, imports and exports of acid from the subsurface compartments to other grid cells were assumed negligible. The soil layer is usually a few inches to a foot deep. The unsaturated zone is primarily sand and gravel glacial deposit with some glacial till and is an average of 25 ft deep. The water table aquifer is 100 ft of sand and gravel, and the bedrock is crystalline rock (mostly granite, gneiss) ~ 1000 ft thick.

The acid neutralizing capability of the deep aquifer was neglected relative to the weathering of overburden in the soil and unsaturated compartments. The direction of annual average flow was taken to be from the interflow to the deep aquifer, from the interflow to the surface lakes, and from the surface lakes to the deep aquifers. Further geohydrological studies are needed to confirm this pattern [2].

Equations 3, 4 and 6 contain a term for sources of alkalinity (acid neutralizing capacity) in the overburden and soils, k M V (r_{eq} - r). This term provides a source of alkalinity until the soil's neutralizing capacity or base saturation is exhausted, i.e., r_{eq} = r. Even the surface water sediments can have a significant degree of buffering capacity under certain circumstances [3], but this factor was not included in the preliminary analysis. Soils data were available from the Soil Conservation Service on soil depth, bulk density, sum of the bases, porosity and hydraulic conductivity. The sum of the bases (or base saturation) was utilized as the value for r_{eq} in each soil layer. The other soils information was utilized in estimating the hydrologic balance and residence times for each compartment.

A more appropriate kinetic argument for the buffering capacity of the solid phase should reflect the mechanisms of H^+ sorption, cation exchange and incongruent dissolution. One possible kinetic expression which would demonstrate a gradual exhaustion or breakthrough curve for the solid phase is:

$$\frac{dr}{dt} = k_f[H^+]\,(r_{max} - r) - k_r[B]\,r \qquad (7)$$

where r = equivalents of H^+ sorbed per mass of soil (eq/100 kg)
r_{max} = maximum base cation exchange capacity for H^+ (eq/100 kg)
k_f = rate of H^+ sorption (m^3/eq-yr)
k_r = rate of H^+ exchange with other cations (m^3/eq-yr)
B = export of base cations (eq/m^3)

Steady-State Results

Under steady state conditions, Equations 3–6 reduce to a set of four algebraic equations which are quite easily solvable by substitution. This model was applied to the Upper Wisconsin River Basin, a 2730-mi^2 area near Rhinelander, Wisconsin (Figure 4). Rainfall pH in the vicinity has been

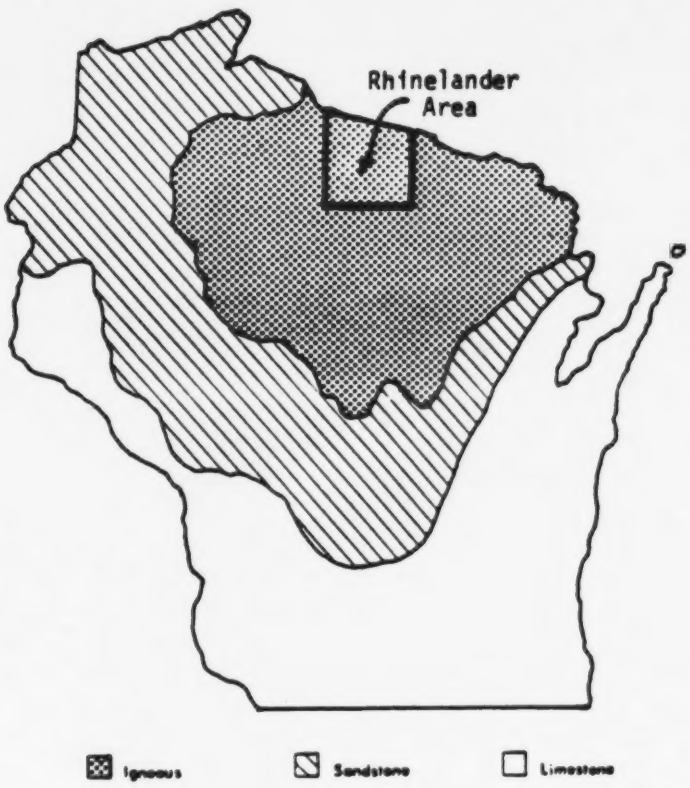


Figure 4. Rhinelander area site map.

averaging ~4.4 (Figure 5). The best estimate at coefficients for this cell using the data from Oakes and Cotter [2] and the SCS are:

V_2	$= 1.55 \times 10^8$ m^3	soil water
V_3	$= 2.59 \times 10^9$ m^3	unsaturated zone water
V_4	$= 8.62 \times 10^9$ m^3	surface lakes
V_5	$= 6.02 \times 10^{10}$ m^3	water table aquifer water
$Q_{2,1}$	$= 4.50 \times 10^9$ m^3/yr	rainfall on land
$Q_{4,2}$	$= 8.95 \times 10^8$ m^3/yr	runoff on lakes
$Q_{3,2}$	$= 8.95 \times 10^8$ m^3/yr	percolation to unsaturated zone
$Q_{5,3}$	$= 1.25 \times 10^9$ m^3/yr	recharge to water table

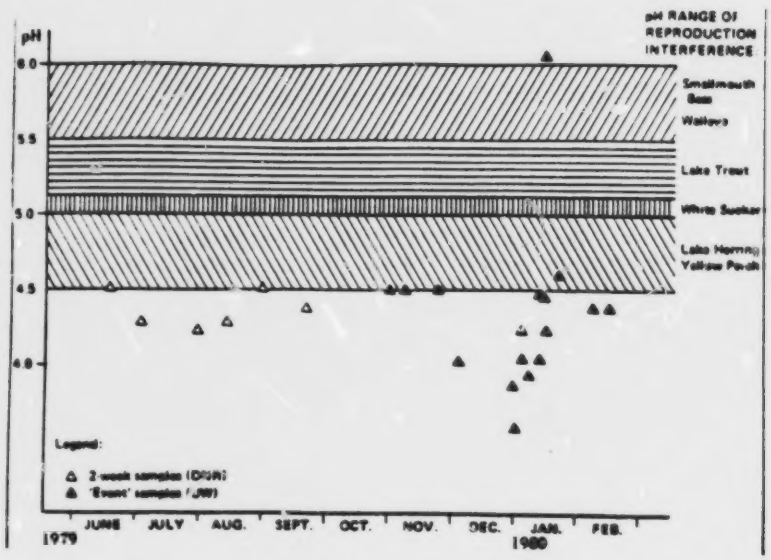


Figure 5. Acid precipitation near Rhinelander (from [4]).

$Q_{3,4}$	= 3.59×10^8 m^3/yr	surface lakes to unsaturated zone
$Q_{4,5}$	= 1.25×10^9 m^3/yr	water table to lakes
$Q_{6,4}$	= 2.23×10^9 m^3/yr	export from surface lakes
$Q_{4,1}$	= 1.12×10^9 m^3/yr	rainfall on lakes
L_{dry}	= 1.42×10^5 kg/yr H^+	dryfall on land
L_{dry}	= 3.55×10^4 kg/yr H^+	dryfall on lakes
A_1	= -3.15×10^{-2} eq/m^3	rainfall alkalinity (pH 4.5)
A_{dry}	= -1.0×10^3 eq/kg	dryfall alkalinity
M_2	= 1.35×10^3 kg/m^3	specific soil density
M_3	= 1.40×10^3 kg/m^3	specific soil density
M_5	= 1.55×10^3 kg/m^3	specific soil density
β_2	= 0.09 in./in.	water capacity in soil
β_3	= 0.06 in./in.	water capacity in unsaturated zone
r_{eq_2}	= 5 eq/100 kg	sum of the bases in soil
r_{eq_3}	= 0.6 eq/100 kg	sum of the bases in unsaturated sands
r_{eq_5}	= 0.1 eq/100 kg	sum of the base in water table sands

Once the alkalinity balance is solved, it is necessary to solve Equation 2 with a root-finding technique in order to determine the pH of each compartment. The partial pressure of CO_2 in the aquifers was assumed to be three times greater than atmospheric in the interflow and ten times greater than atmospheric in the bedrock aquifer compartment.

Results are presented in Table 1, a sensitivity analysis on the weathering rates (represented as the zero-order reactions in Equations 3-6). For the steady-state analysis, it was assumed that the rates of weathering were constant, i.e., the base saturation utilized (r) was not allowed to vary over time. This amounts to an assumption that bases are produced by weathering reactions at the same rate that they are consumed in soil processes. In time-variable simulations, the equivalents of acid neutralized by the soil in weathering reactions is allowed to reach its saturation level r_{eq}. Steady-state results indicate the equilibrium pH values in each compartment for various assumptions on weathering rates. Case 4 is the most realistic according to present field observations in the Upper Wisconsin River Basin. Weathering produces a total of ~ 1200 eq H^+/ha-yr.

Time Variable Results

Equations 3-6 were also solved in a time variable simulation to determine the response of the system and the time required to 95% of equilibrium. The time to equilibrium is strictly a function of the hydraulic detention time and the rate of acid neutralization. The detention times were calculated as:

soil	= 12.6 days
unsaturated zone	= 2.07 years
lakes	= 2.64 years
water table	= 48.2 years

The time required to achieve 95% of the steady state alkalinity after an impulse or a step function change is three times the mean hydraulic detention time of the compartment, but it can be lengthened considerably by the weathering reactions in Equations 3-6.

EVENT MODEL

An event model is needed to simulate the worst case in a lake or stream, such as a snowmelt or rainfall event during fish spawning. Since pH is the variable causing the biological effect, a time-variable pH model is required. Total alkalinity, CO_2, pH and CO_2-acidity are all interrelated. In an open system, total inorganic carbon changes due to gaseous equilibrium of CO_2 (Henry's law). If one knows two of the above chemical concentrations, it is possible to calculate all others at chemical equilibrium. The following is a diffuse source model for acid loading and titration of alkalinity in an open system.

Table 1. Sensitivity Analyses: Changes in Weathering Rates[a]

	Case 1	Case 2	Case 3	Case 4
Weathering Rates	$k_2 = 0$ $k_3 = 0$ $k_5 = 0$	$k_2 = 0.03$ $k_3 = 0$ $k_5 = 0$	$k_2 = 0.03$ $k_3 = 0.001$ $k_5 = 0$	$k_2 = 0.0254$/yr $k_3 = 0.0005$/yr $k_5 = 0.0038$/yr
Soil Compartment	pH = 3.8 Alk = -0.158	pH = 6.1 Alk = +0.0169 Wthr = 554	pH = 6.1 Alk = +0.0169 Wthr = 554	pH = 5.0 Alk = -0.01 eq/m^3 Wthr = 469 eqH$^+$/ha/yr
Unsaturated Zone Compartment	pH = 3.8 Alk = -0.158	pH = 5.8 Alk = +0.007	pH = 6.4 Alk = +0.028 Wthr = 38	pH = 6.5 Alk = +0.0372 eq/m^3 Wthr = 19 eqH$^+$/ha-yr
Surface Water Compartment	pH = 3.8 Alk = -0.158	pH = 4.7 Alk = -0.018	pH = 5.1 Alk = -0.007	pH = 7.5 Alk = +0.124 eq/m^3
Water Table Compartment	pH = 3.8 Alk = -0.158	pH = 5.4 Alk = +0.007	pH = 5.9 Alk = +0.028	pH = 6.9 Alk = +0.320 eq/m^3 Wthr = 626 eqH$^+$/ha-yr

[a]Assumed: dry deposition = 5.5 kg/ha·yr $SO_4^=$ = 177 eq/yr H^+.

Consider the kinetic equations for total inorganic carbon

$$\frac{dC_T}{dt} = K_a ([CO_2]_s - [CO_2]) + S_{C_T} \quad (10)$$

and for the conservative quantity CO_2-acidity defined as

$$CO_2\text{-Acy} = C_T - \text{Alk} \quad (11)$$

so that, by substitution:

$$\frac{d [CO_2 - \text{Acy}]}{dt} = K_a ([CO_2]_s - [CO_2]) + S_{CO_2\text{-Acy}} \quad (12)$$

where S_{C_T} and $S_{CO_2 - \text{Acy}}$ are the external sources and sinks of total inorganic carbon and CO_2-acidity that may exist. K_a is the CO_2 rate constant for gas exchange and can be estimated from the O'Connor and Dobbins [5] reaeration formula. Wet and dry depositional loadings are included in the source term, S_{C_T} and $S_{CO_2 - \text{Acy}}$. For low pH, it is clear from the chemical equilibria that:

$$C_T = [CO_2] + [HCO_3^-] + [CO_3^=] \simeq [CO_2]$$

And since $CO_2\text{-Acy} = [CO_2] - [CO_3^=] - [OH^-] + [H^+]$ there exists a pH range for which $CO_2\text{-Acy} \simeq [CO_2]$. The accuracy of these approximations is within 10% and acceptable for most engineering purposes (Figure 6). For $pH \leq 4.3$, the total inorganic carbon equation (1) can be written using $C_T \simeq CO_2$ with the result:

$$\frac{d [CO_2]}{dt} = K_a ([CO_2]_s - [CO_2]) + S_{C_T} \quad (13)$$

For $4.3 \leq pH \leq 7.5$, the CO_2-acidity equation (12) can be written

$$\frac{d [CO_2]}{dt} = K_a ([CO_2]_s - [CO_2]) + S_{CO_2\text{-Acy}} \quad (14)$$

These equations form the basis for the analysis of a wide range of acidity problems in natural waters since they are linear in CO_2 and therefore are easily solved. Once the CO_2, C_T, and/or CO_2-Acy concentrations are known, the pH may be calculated from equilibrium considerations.

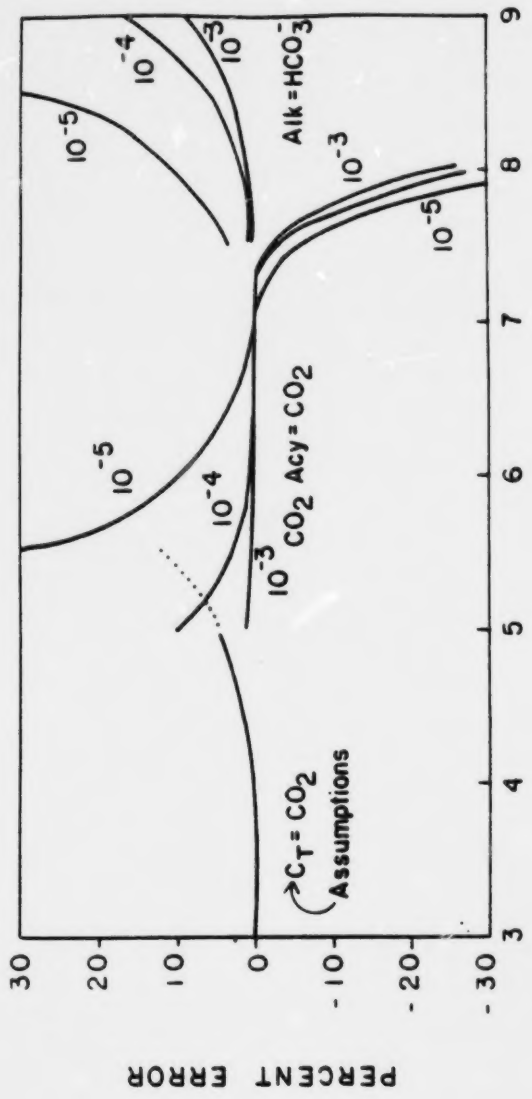


Figure 6. Percentage error vs pH.

For pH > 7.5 the differential equation is still represented by:

$$\frac{dC_T}{dt} = K_a ([CO_2]_s - [CO_2]) + S_{C_T} \quad (15)$$

However, in this pH range, neither the approximation:

$$C_T \simeq [CO_2]$$

nor

$$[CO_2\text{-Acy}] \simeq [CO_2]$$

is appropriate. The equation is nonlinear because CO_2 is a function of C_T, alkalinity, carbonate anion and pH.

Since it can be shown that:

$$[CO_2] = C_T - Alk + CO_3^{=} - H^+ + OH^- \quad (16)$$

we may substitute for $[CO_2]$ in the differential Equation 15. Assuming no external sources or sinks, the change of total inorganic carbon with respect to time is:

$$\frac{dC_T}{dt} = K_a ([CO_2]_s - C_T - \phi(t)) \quad (17)$$

where $\phi(t) = -Alk + CO_3^{=} - H^+ + OH^-$. ϕ is calculated from the total acid loadings to the ecosystem by direct runoff and tributary inputs.

If a stream or river is divided into sufficiently short segments such that the alkalinity and pH can be considered constant, Equation 17 is simply a first-order, linear differential equation with constant coefficients. The solution is:

$$C_T = C_{T_0} \exp(-K_a t) + ([CO_2]_s - \phi)(1 - \exp(-K_a t)) \quad (18)$$

where

$$\phi = -Alk + CO_3^{=} - H^+ + OH^-$$
$$[CO_3^{=}] = K_a[Alk]/[H^+]$$

Once C_T is known, carbon dioxide and pH may be calculated from Equation 16.

In the expression for carbonate, the assumption is made that alkalinity is approximately equal to the bicarbonate ion. The assumption restricts the analysis to pH <9.0, but this pH range includes most values found in natural waters. The error in the assumption is given in Figure 6.

An excellent hypothetical example of increasing pH and degasification after an acid rainfall event is presented in Figure 7. Actual data of this sort were not available, but an example problem at nearly neutral pH was found.

Example Problem: Madison River

The diurnal pH at six sampling stations for the Madison River in Yellowstone Park was reported by Wright and Mills [7]. The data at 6:00 a.m. provided an example of stream data at pH <8.0. Field CO_2 concentrations were calculated from the pH and alkalinity data. To solve the differential equation (12) the assumption was made that CO_2-Acy = CO_2. The respiration measurements of Wright and Mills were included in the analysis and the solution to the CO_2 deficit equation was:

$$D = D_0 \exp(-K_a t) - \frac{P-R}{HK_a}\{1 - \exp(-K_a t)\} \tag{19}$$

where

D = CO_2 deficit
P = production sink of CO_2
R = respiration source of CO_2 (Table 2)
H = mean depth
t = travel time

Table 2. Madison River Segment Parameters

x (mi)	$\bar{U}$ (mi/day)	H (m)	Ka (day^{-1})	R (g/m^2-day)
1.56	30.6	0.59	6.65	1.0
3.64	19.1	1.09	2.13	0.4
6.60	29.6	0.44	10.2	0.0
9.66	36.2	0.36	15.1	0.1

The solution to Equation 19 using the O'Connor and Dobbins [5] reaeration formula to compute K_a is presented in Figure 8. Note the reasonable fit of the model to the field data.

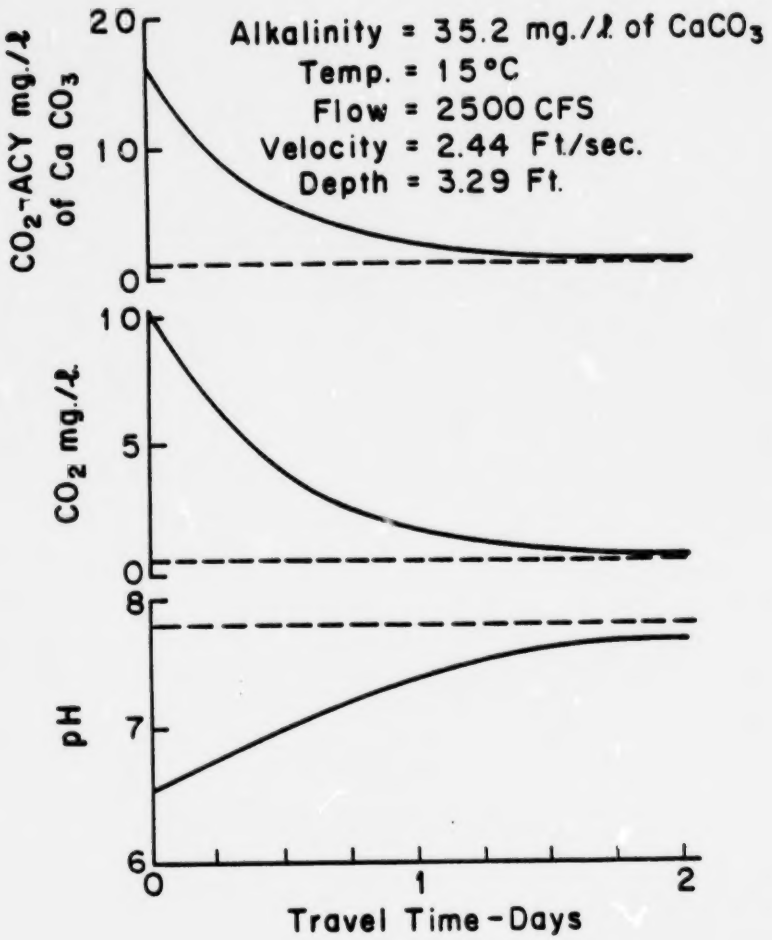


Figure 7. CO_2 exchange after acidification (from [6]).

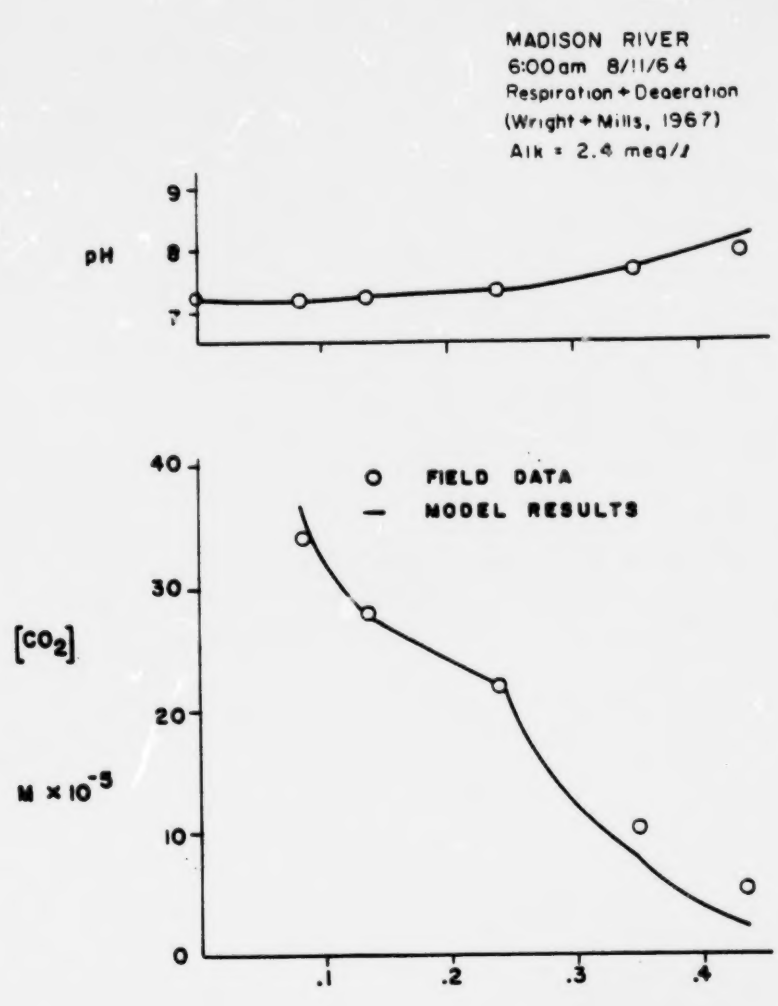


Figure 8. Madison River example.

CONCLUSIONS AND RECOMMENDATIONS

The trickle-down model proved to be a conceptual approach of significant value in a regional acid rainfall assessment. Much more effort is needed if it is to be used as a predictive tool. Specifically we plan to improve the weathering rates and kinetics and eventually to link the model into an atmospheric transport grid system. Metal dissolution and nutrient availability questions could be addressed within the constructs of this mass balance approach.

The simplifications introduced into the acid rainfall event model aided in solving a rather complex problem. With sufficient field data, it should be possible to calibrate and verify this model.

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